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Surface properties of Mo-implanted PVD TiN coatings using MEVVA source

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ABSTRACT

To further improve the tribological properties of TiN coatings used on mechanical parts, Mo ions were implanted into PVD TiN coatings with Metal Vapor Vacuum Arc (MEVVA) source at the implantation dose as high as 1×10^{18} ions/cm^2. Surface morphology, microstructures, and nano-hardness of TiN coatings were investigated by optical profilometer, X-ray diffraction (XRD), X-ray photoelectron spectroscope (XPS), and Nano Indenter System. The tribological properties were investigated on a ball-on-disk friction and wear tester. The XRD results demonstrated that the diffraction peak of Ti_2N appeared in the Mo-implanted TiN coatings. However, there was obvious decrease of nano-hardness due to the soft Molybdenum phase and its oxides. It was approved that Mo-implanted TiN coatings could greatly improve their tribological properties and that the implantation at dose of 1×10^{18} ions/cm^2 could result in much lower friction coefficient. The existence of soft molybdenum, lubricious molybdenum oxides and titanium oxides resulted in the remarkable reducing of the friction coefficient of TiN coatings with Mo-implantation.

1. Introduction

Titanium nitride (TiN) coatings have been used as wear resistant coatings for cutting tools and dies owing to their high hardness, good wear and corrosion resistance. In recent years, TiN coatings started to be used on machine parts like automobile parts and in some industries which required low friction [1–5]. As a result, low friction coefficient becomes essential to TiN coatings. Therefore, some studies have been carried out to investigate friction coefficients of TiN coatings. Azushima et al. [2,3] studied the influences of preferred grain orientations on friction coefficients of TiN coatings with different counter ball materials under dry condition. They revealed that a (1 1 1) preferred grain orientation could obtain a lower friction coefficient than a (2 0 0) preferred grain orientation for TiN coatings when the counter ball materials are SUJ2, SUS304, SUS440C and SWRM10. And they proposed that titanium oxide film on the contact surface of counter balls for TiN coatings with the (1 1 1) preferred grain orientations resulted in lower friction coefficients. On the other hand, lots of ions like C, N, Al, V and Zr [6–10] were implanted into TiN coatings and showed obvious effects on improving tribological performance of TiN coatings. As a result, ion implantation has been proved to be an effective way to improve the tribological properties of TiN coatings. However, there were few studies of Mo ion implantation on tribological properties of TiN coatings. Deng, et al. [11] investigated the effects of Mo and Mo+C ion implantations on PVD TiN coatings. They reported that nano fiber phase rich in Mo was found in TiN coatings after Mo implantations and that higher implantation dose could enhance the hardness, and decrease the wear rate and friction coefficient. Thus, it is possible to obtain much lower friction coefficient of TiN coatings by further increasing Mo ion implantation dose. This is because besides forming some special microstructure, higher implantation dose may provide more Mo element which may produce more molybdenum oxides with Magneli phase structure [12,13] as lubricant under dry friction. However, the dose of Mo ion implantation in the former study [11] was no more than 4.5×10^{17} ions/cm^2. Moreover, there were lack of further studies on the surface morphology and worn surfaces, which were very critical for TiN coatings with Mo implantation applied on machine parts and in relevant industries.

In this paper, Mo ions with dose as high as 1×10^{18} ions/cm^2 are implanted into PVD TiN coatings with MEVVA source. The microstructure, surface morphology and mechanical properties of TiN coatings are investigated. Ball-on-disk sliding friction and wear tests are carried out to investigate their tribological properties,

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especially Mo implantation effects on friction coefficients and worn surfaces. The wear mechanism of the Mo-implanted TiN coatings is also proposed.

2. Experimental methods

All substrate samples were made from 316L stainless steel with dimensions of 70 mm × 30 mm × 1 mm with Ra of 4.13 nm and the hardness of 150 $HV_{0.2}$. After ultrasonically cleaned for 15 min with acetone and alcohol, respectively, about 1.6 μm thick PVD TiN coatings were deposited on the surface of substrate samples by an MIP-10-800 Multi Arc Ion Plating. The parameters of TiN deposition included a nitrogen pressure of 0.6 Pa, an arc current of 60 A, a duty cycle of 30%, a temperature of 200 °C, a substrate bias of 200 V, and TiN deposition for 90 min after Ti deposition for 5 min. Before Mo ion implantation, the TiN coating samples were again ultrasonically cleaned for 15 min with acetone and alcohol, respectively. Then a MEVVA II A-H source, made by Beijing Normal University, China, was utilized to implant Mo ions into the TiN coatings. The parameters of Mo-implantation included a vacuum of 2×10^{-4} Pa, an average ion energy of 80 keV, a current density of 24 $\mu A/cm^2$, and an accelerating voltage of 26 kV. The implantation temperature was room temperature at the beginning and without heating in the whole process. To further control the surface temperature lower than 100 °C during the whole implantation, the sample surfaces of TiN coatings were kept out of implantations for 10 min by a sample shutter every 20 min. And the two doses of Mo ion implantation were 3×10^{17} ions/cm^2 and 1×10^{18} ions/cm^2 (corresponding to the 3E17 and 1E18 in the following part of the paper, respectively).

NanoMap-D optical profilometer was used to measure surface morphology of TiN coatings and their roughness. PHI-710 scanning Auger microprobe (SAM) was adopted to detect the Mo element profile on the TiN coating surface and it was found that the implantation depth was about 200 nm. ESCALAB 250 X-ray photoelectron spectroscope (XPS) was employed to analyze the chemical states of the elements of the coating surfaces after sputter for 10 nm by Ar ions. D/max-2500 X-ray diffraction (XRD) with 2° incidence angle of fixed omega was utilized to characterize the phases of the surface coatings. Nano-hardness and elastic modulus of the samples were surveyed by MTS XP Nano Indenter System with a Berkovich indenter tip in the Continuous Stiffness Mode (CSM).

Friction and wear tests were conducted on an MS-T 3000 ball-on-disk friction and wear tester with a 4 mm diameter Si_3N_4 ball sliding on the TiN samples under an applied load of 1.96 N. The ball was static while TiN coating disk was rotating during the dry friction driven by a motor. The tests were carried out at a sliding velocity of 0.126 m/s with the wear track radius of 3 mm for 60 min under dry friction in air. The room temperature was 20 ± 3 °C and the relative humidity was 45 ± 5%. The volumes of wear tracks were measured by the NanoMap-D optical profilometer and the Scanning Probe Image Processor (SPIP) software, and calculated by the following formula:

$$V = \frac{V_1}{L_1} \times \pi \times d$$

where V is the total wear volume of the wear tracks (μm^3); L_1 is the arc length of a part of the wear tracks (μm); V_1 is the wear volume of the part of wear track with the arc length of L_1 (μm^3); and d is the wear track diameter (μm).

Then the wear volumes were calculated into wear rates. JEOL JSM-7001F scanning electron microscope (SEM) and Energy-Dispersive X-ray Spectrometer (EDS) were used to analyze the morphologies and element distribution of the worn surfaces of samples.

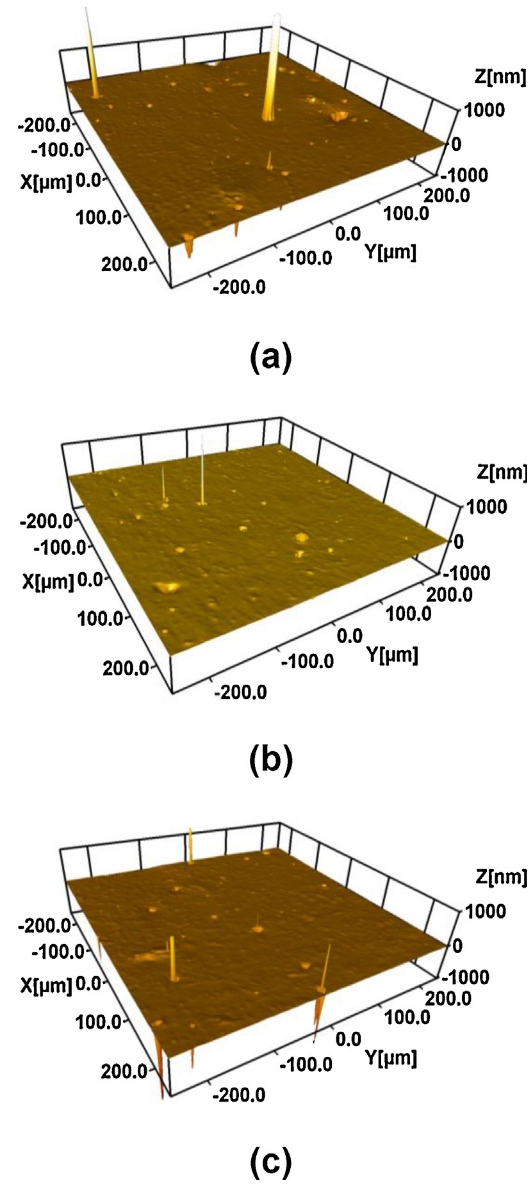

Fig. 1. Morphology of the TiN coating surfaces with different Mo implantation doses (a) un-implanted; (b) 3E17; and (c) 1E18.

3. Results and discussion

3.1. Characterization

Mo implantations can obviously change the surface color of TiN coatings from golden yellow to silvery white with a little light yellow for TiN coatings with Mo dose of 3E17 and to bright silvery white for TiN coatings with Mo dose of 1E18, by naked-eye observation. Fig. 1 shows the three-dimension morphology of the TiN coating surfaces with different Mo implantation doses. It can be seen that there are several droplets and pits on all TiN coatings. However, droplets are a little smaller after Mo implantation due to the sputter effect on PVD TiN surfaces during the implantation process. Furthermore, their roughness with a measuring area of 0.5 mm × 0.5 mm is listed in Table 1. The results show that Mo implantations do not cause increase of surface roughness of TiN coatings. And from the results of morphology and roughness, it can be seen that Mo implantation may not result in higher friction coefficients and is beneficial to TiN coatings used in machine parts.